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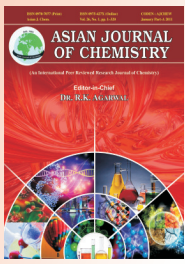

Vibrational Spectroscopic Study of Two Dimensional Polymer Compounds of 5-Aminouracil

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In this study, FT-IR and FT-Raman spectra of two dimensional coordination polymer compounds, $M(5AU)_2Ni(CN)_4$ (where M = Mn, Co, Ni, Zn and Cd; 5AU = 5-aminouracil *i.e.*, 5-amino-2,4-dihydroxypyrimidine) were reported. 5-Aminouracil molecules are found to involve coordination through one of the pyrimidine ring nitrogen atoms. The spectral features suggest that the compounds are similar in structure to the Hofmann type two dimensional coordination polymer compounds, formed with $Ni(CN)_4^{2-}$ ions bridged by $M(5AU)_2^{2+}$ cations. Vibrational bands originated from both 5AU and $Ni(CN)_4$ group were assigned.

Keywords: FT-IR and Raman spectra, Hofmann type complexes, Tetracyanonickelate, 5-Aminouracil.

INTRODUCTION

Uracil and its derivates, constituents of the genetic materials, play a fundamental role in basic biological process. 5-Substituted uracils exhibit significant pharmacological activity and they are used as antitumor, antibacterial and antiviral drugs, being therefore the most interesting and studied uracil[1]. Among the 5-subsituted uracil, 5-aminouracil (5-amino-2,4-dihydroxypyrimidine) plays special attention. It is a pyrimidine nucleobase analogue of thymine in which the methyl group is replaced by amino group, adding therefore new hydrogen bonding sites. 5-Aminouracil has been used as a starting material for the synthesis of other pyrimidines[2-4] or transition metal complexes[5].

The well known Hofmann-type two dimensional complexes, $\{M(L)_2Ni(CN)_4\}$, are built by stacking the two dimensional nickel cyanide sheets in layers[6,7]. The two-dimensional sheet is constructed by the alternate linkage between square-planar Ni(II) and octahedral M(II) (M = Mn, Fe, Co, Ni, Cu, Zn or Cd) through the cyanide bridges. The octahedral coordination of M(II) is satisfied by four N-terminals of the cyano groups and two nitrogen atoms of the two N-donor ligands (L) in a *trans* configuration, protruding above and below the sheet[6,7]. In this study, 5-aminouracil tetracyanonickelate, $M(5AU)_2Ni(CN)_4$ {where M = Mn, Co, Ni, Zn or Cd; 5AU = 5-aminouracil, abbreviated hereafter as M-Ni-5AU}, coordination polymer compounds have been prepared for the first time and their FT-IR (4000-400 cm^{-1}) and FT-Raman (4000-50 cm^{-1}) spectra are reported. These complexes are an example of two dimensional coordination polymers in tetracyanometallate-bridged systems. The aims of this study are to examine the coordination sensitive ligand modes and to determine vibrational wavenumbers of modes arising from metal-ligand bonds $\{(M\text{-}N)_{5AU}, \delta\ (N\text{-}M\text{-}N)_{5AU}\}$ by studying isostructural complexes $\{M(5AU)_2Ni(CN)_4\}$.

EXPERIMENTAL

All chemicals used were reagent grade (Aldrich) and they were used without further purification. The complexes M-Ni-5AU (M = Mn, Co, Ni, Zn or Cd) were prepared as following: at first 1 mmol of MCl_2 was dissolved in the distilled water, then to this solution 1 mmol of $K_2Ni(CN)_4$ dissolved in distilled water was added under stirring. After a short time slightly more than 2 mmol of the 5-aminouracil solution in alcohol were added to the mixture prepared drop wise, again under stirring. The final mixture was left for stirring around a week at room temperature. The obtained product was filtered and washed with water, ethanol and ether successively and dried in a desiccator which included P_2O_5.

The freshly prepared compounds were analyzed for C, H and N by a LECO CHNS-932 analyzer with the following results [found (calcd.) %]: $Mn(C_4H_5N_2O_2)_2Ni(CN)_4$: C= 29.98 (30.54), H = 2.35 (2.13), N = 28.76 (29.68); $Co(C_4H_5N_2O_2)_2Ni(CN)_4$: C = 30.02 (30.28), H = 2.43 (2.11), N = 29.22 (29.43); $Ni(C_4H_5N_2O_2)_2Ni(CN)_4$: C = 30.25 (30.30), H = 2.03 (2.11), N = 29.11 (29.44); $Zn(C_4H_5N_2O_2)_2Ni(CN)_4$: C = 29.43 (29.88), H = 2.35 (2.08), N = 29.11 (29.03); $Cd(C_4H_5N_2O_2)_2Ni(CN)_4$: C = 27.13 (27.22), H = 1.87/1.90, N

= 26.39 (26.45). The analytical results were agreement with the proposed formula.

Physical measurements: FT-IR (4000-400 cm^{-1}) spectra between KBr windows as Nujol or hexachloro-1,3-butadiene mulls and far-infrared (600-50 cm^{-1}) spectra between polyethylene plates as Nujol mulls of the compounds were recorded *via* a Bruker Optics IFS66v/s FT-IR spectrometer with 2 cm^{-1} resolution in vacuum. FT-Raman spectra of the compounds were recorded using a Bruker Senterra Dispersive Raman microscope spectrometer with 532 or 633 nm excitations from a 3B diode laser having 3 cm^{-1} resolution in the region of 3700 and 60 cm^{-1}.

RESULTS AND DISCUSSION

The structural formula of 5-aminouracil is given Fig. 1. The FT-IR and FT-Raman spectra of $M(5AU)_2Ni(CN)_4$ (where M = Mn, Co, Ni, Zn and Cd) are found to be very similar, suggesting that they have isomorphous crystal structures. The FT-IR and FT-Raman spectra of the $M(5AU)_2Ni(CN)_4$ (where M = Mn, Co, Ni, Zn and Cd) complexes are given in Figs. 2 and 3. The assignments were divided into two groups arising from the 5-aminouracil, the $Ni(CN)_4$ ions.

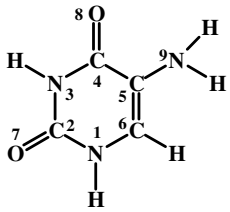
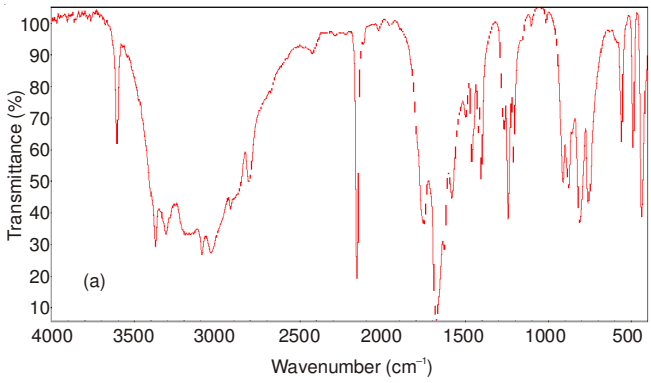
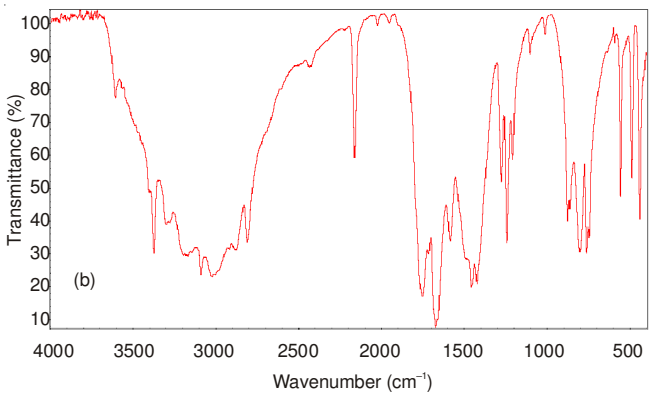
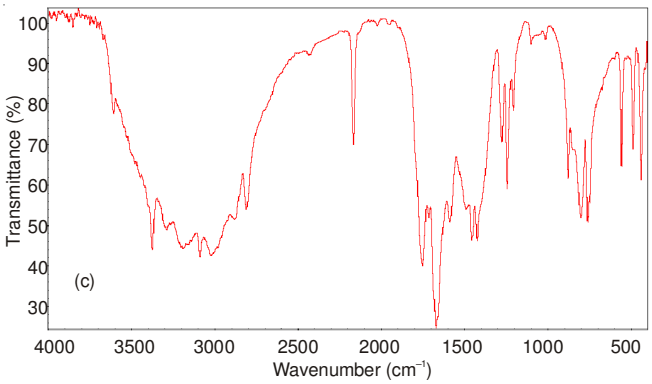
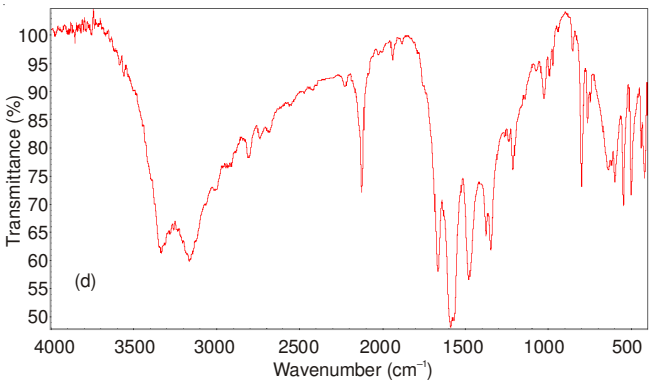


Fig. 1. Structural formula of 5-aminouracil









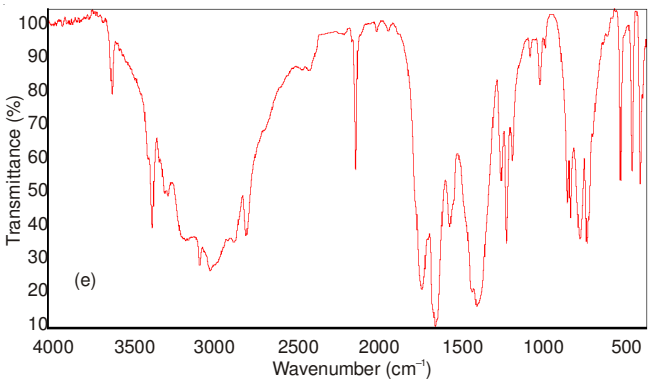


Fig. 2. FT-IR spectra of Hofmann-5AU compounds in KBr: (a) Mn-5AU-Ni, (b) Co-5AU-Ni, (c) Ni-5AU-Ni, (d) Zn-5AU-Ni and (e) Cd-5AU-Ni

5-Aminouracil (5AU) vibrations: The detailed vibrational assignments for 5-aminouracil were made by Palafox *et al.*[8] and Singh[9] where they reported the calculated and experimental frequencies of 5-aminouracil. The 36 fundamental modes of 5AU may be classified according to the molecular point group Cs into 25A' symmetry species (in-plane) and 11A" species (out-of-plane). Since all the vibrations are IR and Raman active, the absence of Raman spectra present no serious difficulty.

5-Aminouracil has different sites, therefore, has different binding modes. It can coordinate through one of the pyrimidine ring nitrogen, the C=O and/or-NH_2 groups. Therefore, vibrational wavenumbers of 5AU in M-Ni-5AU complexes studied are carefully investigated.

If the coordination occurs through the amino nitrogen atom, it is expected that a great reduction would take place in the NH_2 stretching NH_2 bending and C-NH_2 stretching wavenumbers and when coordination occurs through the oxgen of carbonyl group, negative shift at ν(C=O) mode of coordinated

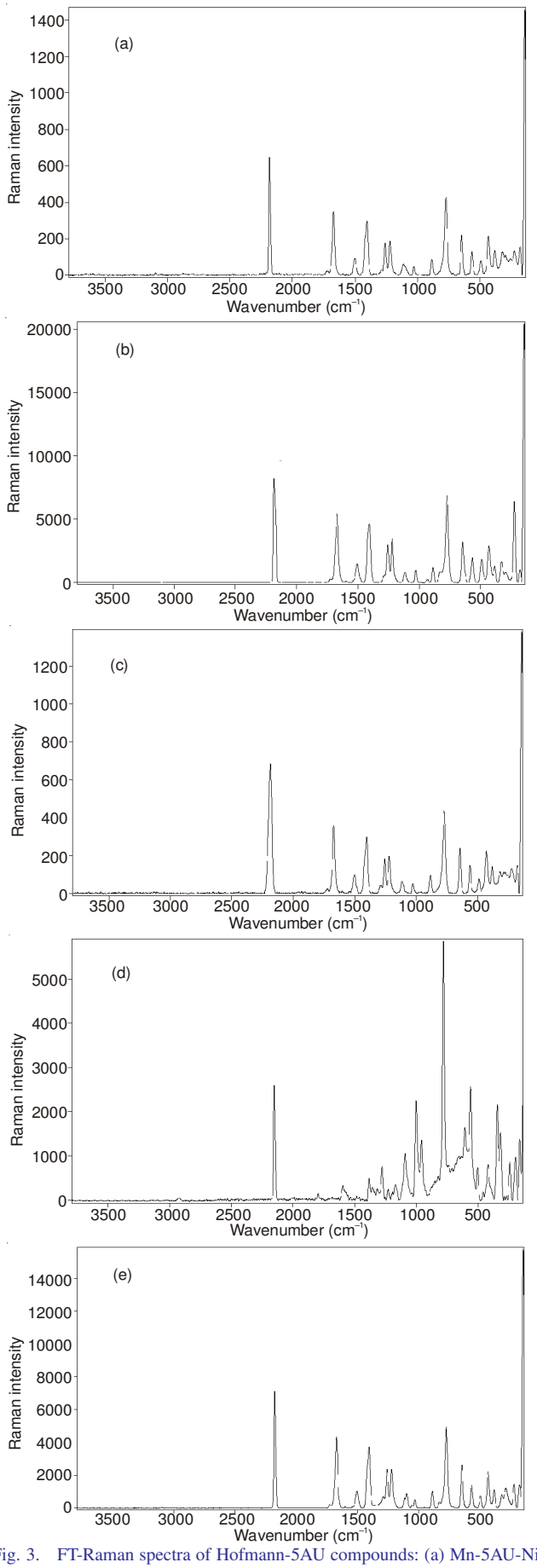


Fig. 3. FT-Raman spectra of Hofmann-5AU compounds: (a) Mn-5AU-Ni, (b) Co-5AU-Ni, (c) Ni-5AU-Ni, (d) Zn-5AU-Ni and (e) Cd-5AU-Ni

molecule with respect to the free ligand is expected[7,10,11]. On the other hand when the aromatic ring nitrogen involves in complex formation, certain ring modes are affected[11]. In order to determine the coordination site of 5-aminouracil in $M(5AU)_2Ni(CN)_4$ (M = Mn, Co, Ni, Zn and Cd) complexes, the wavenumbers of 5-aminouracil in complexes are compared with those of free 5-aminouracil. Some selected fundamental modes of complexes are reported in Table-1. The spectroscopic results indicated that the amino group hydrogen bonding interaction in comparison with those of other M-Ni-5AU complexes.

We observed four broad bands corresponding to stretching vibrations $\nu(NH_2)$ and their wave numbers are found to be higher in value than those of free 5-aminouracil[10-13]. A positive shift of these absorptions is usually regarded as signifying that the ligand is not NH_2-bonded. This band indicates the presence of 5-aminouracil in $M(5AU)_2Ni(CN)_4$ (M = Mn, Co, Ni, Zn and Cd) complexes in its amine form and the rather broad character of the NH_2 vibration bands is suggestive of H bond participation[12-14]. In addition, NH_2 scissoring mode of 5-aminouracil is observed at 1670 cm^{-1} for 5-aminouracil and around 1671 cm^{-1} for complexes. These results suggested that the NH_2 groups of 5-aminouracil are not involved in the coordination with the metal ions and are in good agreement with those reported in the literature[15,16].

The ν(C=O) mode is observed at 1755 cm^{-1} for solid 5AU and around 1754 cm^{-1} in the FT-IR spectra of complexes, indicating that the ligand not coordinate to the metal ions through (C=O) group. These bands at 1450, 1298, 1240, 1080, 1010 and 740 cm^{-1} in the FT-IR spectra (at 1465, 1310 and 1080 cm^{-1} in the FT-Raman spectra) with ring contribution exhibit intensity changes and shift to higher wavenumbers in complexes. On the other hand, the in-plane bending mode (1580 cm^{-1} IR) in M-Ni-5AU complexes show upward frequency (1587 cm^{-1} FT-IR, respectively) shift compared to those of free 5AU molecules. All of these data suggest binding between the metal(II) and the ring N atom of the 5-aminouracil. Analogous shifts on coordination were observed in 6-aminouracil,[17] creatinine[18], pyrazinamide[19], 2-aminopyrimidine[20], 4-aminopyrimidine[20,21] complexes and are explained as the coupling of the internal modes of the aromatic molecule with the M-N vibrations[17-21].

$Ni(CN)_4$ group vibrations: The vibrational wavenumbers of the $Ni(CN)_4$ group for the complexes studied are given in Table-2 together with those Hofmann type clathrates[22-24] and $K_2Ni(CN)_4$[11,23] for comparison. As seen in Table-2, the vibrational wavenumbers of $Ni(CN)_4$ groups are found to be much higher than those of $Ni(CN)_4$ in $K_2Ni(CN)_4$ salt. The higher wavenumbers in M-Ni-5AU, compared to the free $Ni(CN)_4$, are caused by coordination of tetracyanonickelate ion, through the nitrogen atoms to metal (M). Such upward wavenumber shift have been observed for Hofmannn type clathrates[24] and pyrazinamide complexes $M(PZA)_2Ni(CN)_4$ (M = Mn, Co, Ni, Zn or Cd; PZA = pyrazinamide)[18], in which both ends of the CN group are coordinated and explained as the mechanical copuling of the internal modes of $Ni(CN)_4$ with the M-NC vibrations[18]. The Raman active cyanide stretching modes of M-Ni-5AU (M= Mn, Co, Ni, Zn and Cd) complexes are shown

TABLE-1
VIBRATIONAL VAWENUMBERS (cm^{-1}) OF 5-AMINOURACIL IN THE M-Ni-5AU COMPLEXES

Sym.	Assignments[a]	5-Aminouracil [a] IR	5-Aminouracil [a] Raman	Mn-5AU-Ni IR	Mn-5AU-Ni Raman	Co-5AU-Ni IR	Co-5AU-Ni Raman	Ni-5AU-Ni IR	Ni-5AU-Ni Raman	Zn-5AU-Ni IR	Zn-5AU-Ni Raman	Cd-5AU-Ni IR	Cd-5AU-Ni Raman
A'	$\nu_{as}(NH_2)$	3380s	-	3375s	–	3376s	–	3375s	–	3336s	–	3377s	–
A'	$\nu_{s}(NH_2)$	3290m	-	3310s	–	3299s	–	3292m	–	3313s	–	3303s	–
A'	$\nu(N_1H)$	3180sh	3180s	3180s	–	3199s	–	3193s	–	3167s	–	3173s	–
A'	$\nu(N_3H)$	3125mw	3125s	3140s	–	3141s	–	3139s	–	3139s	–	3140s	–
A'	$\nu(C_6H)$	3070sh	3065ms	3093s	–	3093s	3097vw	3091s	–	3066s	–	3091s	–
A'	$\nu(C_2{=}O_7)$	1755s	1755ms	1755s	–	1755s	–	1753s	–	1754s	1797w	1754s	–
A'	$\nu(C_4{=}O_8)$	1715sh	1715w	–	–	1717msh	–	1715msh	–	–	–	1717msh	–
A'	$\beta(NH_2)$	1670s	1675m	1671vs	1671m	1672vs	1671m	1672vs	1671m	1668vs	–	1671vs	1671m
A'	$\nu(C_5{=}C_6)$ ring	1650s	1645m	–	–	1661ssh	–	1660ssh		1659ssh	–	1662ssh	–
A'	$\beta(N_1H)$	1580s	1580s	1584s	1505w	1587s	1502w	1587s	1502w	1587s	1594vw	1585s	1502w
A'	ν (ring)	1450vs	1465m	1463m	–	1459m	–	1460m	–	1480m	1484vw	1452m	–
A'	$\beta(N_3H)$	1420vs	1420s	1425w	–	1424w	–	1424w	–	1380m	1385w	1424w	–
A'	$\nu(C_5\text{-}NH_2)$	1365w	–	1405m	1407m		1405m	–	1404m	1348m	1354vw	–	1404m
A'	ν(ring)	1298vs	1310s	1267w		1276m	1284vw	1277w	–	1262m	1317vw	1276m	–
A'	ν(ring) kekule	1240vs	–	1244s	1256m	1245s	1258m	1246s	1257m	1240s	1276m	1244s	1256m
A'	$\beta(C_6H)$	1205s	–	1211m	1220m	1208m	1220m	1208m	1220m	1213m	1229m	1210m	1220m
A'	$\rho(NH_2)$	1100ms	1105ms	1104vw	1116w	1102vw	1113w	1102vw	1117w	1115vw	1119w	1102vw	1115w
A'	ν (ring)	1080sh	1075ms	–	–	–	–	–	–	1029w	1091m	1043w	
A'	α(ring)	1010m	–	1015vw	1027w	1013vw	1028w	1013vw	1028w	995vw	1027w	1012vw	1028w
A"	$\gamma(C_6H)$	980w	975ms	913s	–	–	–	–	–	973vw	1002vs	–	–
A"	$\gamma(N_3H)$	885vs	885m	873s	886w	877s	884w	878s	886w		956m	877s	885w
A"	$\gamma(N_1H)$	843m	840ms	813vs	–	864m	–	854msh	–	853w	824w	860vs	–
A"	$\gamma(C_2{=}O_7)$	795s	785ms	–	–	802vs	–	802vs	–	800vs	–	801vs	–
A"	$\gamma(C_4{=}O_8)$	768vs	–	760vs	772s	760vs	773s	761vs	773s	763vs	780vs	760vs	772s
A'	ν(ring) breathing	740sh	–	749sh		747sh	–	748sh	–	747sh	–	749sh	–
A'	α (ring)	655w	655s	–	645m	–	646m	673wsh	645m	–	652m	–	645m
A"	δ(ring)	600sh	605w	–	–	590vw	–	599vw	–	638w	606m	635vw	
A"	$\gamma(C_2{=}O_7)$	555vs	–	560s	566m	557s	565m	558s	563m	548s	559m	557s	565m
A"	$\gamma(C_4{=}O_8)$	530sh	520s	–	–	–	–	–	–	–	–	–	–
A"	$\omega(NH_2)$	485vs	–	488s	489w	488s	492w	488s	491w	501vs	503vw	488s	492w
A"	$\tau(NH_2)$	430vs	430ms	–	430m	–	430m	–	430m	–	419m	–	430m
A'	α (ring)	410sh	–	–		–		415vw		418s	–	424wsh	
A"	δ (ring)	380ssh	–	–	382w	–	381w	–	381w	–	–	–	381w
A"	δ (ring)	280s	283ms	–	283w	–	294w	–	289w	–	286w	–	284w
A'	$\beta(C_5\text{-}NH_2)$	230vs	–	–	–	–	–	–	–	–	–	–	
A"	$\gamma(C_5\text{-}NH_2)$	205vs	–	–	221s	–	222s	–	223s	–	195m	–	221m

[a]Taken from Ref.- 9, Abb: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; ν, stretching; s, symmetric; as, antisymmetric; α, angle bending; β, in-plane bending; γ, out-of-plane bending; τ, torsion/twist; ρ, rocking; ω, wagging; δ, out-of-plane ring deformation or ring torsion.

TABLE-2
VIBRATIONAL WAVENUMBERS OF TETRACYANONICKELATE GROUP AND METAL-5AU VIBRATIONS

Assignment	$K_2Ni(CN)_4$[a]	$M(NH_3)_2Ni(CN)_4$ 2Bz[b] M = Mn	$M(NH_3)_2Ni(CN)_4$ 2Bz[b] M = Cd	M-Ni-6AU[c] Mn	M-Ni-6AU[c] Cd	M-Ni-6AU[c] Mn	M-Ni-5AU Co	M-Ni-5AU Ni	M-Ni-5AU Zn	M-Ni-5AU Cd
$\nu(CN)\ E_u$	2124[d]	2152[e]	2156[e]	2158s	2161vs	2159s	2162vs	2165vs	2165vs	2162vs
–	–	–	–	–		–	–	–	–	–
$\nu(Ni\text{-}CN)\ E_u$	538	544	554	545m	545m	544m,sh	541m,sh	529vw	–	535w
$\pi(NiCN),\ A_u$	444	448	446	–	–	–	–	–	–	–
$\delta(NiCN)\ E_u$	419	428	425	437s	430s	438s	441s	441s	441s	441s
$\nu(CN)\ A_g$	–	–	2175	2186vs	2181vs	2184 vs	2185vs	2183vs	2188vs	2173vs
$\nu(CN)\ B_g$	–	–	2164	–	–	–	–	–	–	–
$\nu(Ni\text{-}CN)A_g$	405	462-477	445-450	–	–	–	–	–	457w	–
$\delta(NiCN)E_g$	302	312-322	305-307	316m	326w	328vw	319vw	348vw	344s	326w
$\nu(M\text{-}L)_L$	–	200-206	190-192	226w	210sw	283w	256vw	232vw	240m	216s
$\delta(NMN)_L$	–	176[d]	160[d]	–	149vs	177w	177w	179w	160m	174m

[a]Taken from Ref.[23]. [b]Hofmann type clathrates $M(NH_3)_2Ni(CN)_4.2G$ where G is either zero (host lattice) or the guest molecule (benzene or thiophene) taken from Refs.[22,23]. [c,d,e]Taken from Refs. [18,24,11], respectively. vs: very strong, s: strong, m: medium, w: weak, vw: very weak and sh: shoulder.

in Fig. 2. The presence of just two ν(CN) Raman active bands and one IR active bands confirm that nickel atoms have a square planer enviroment. FT-Raman bands below 300 cm^{-1} region is assigned based on the comparison with the Raman spectra of Hofmann type clathrates and tetracyanonickelate complexes[22,23] where available. FT-Raman spectral investigation of M-Ni-5AU complexes enable us the determine coordination mode of 5AU. As seen in Table-2, the vibrational modes of $\nu(M\text{-}L)_{5AU}$ and $\delta(NMN)_{5AU}$ are found to close where expected for ν(M-L) and $\delta(NMN)_L$ (L = NH_3) for Hofmann type clathrates, which confirms coordination of 5AU through ring nitrogen.

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